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UNDERGROUND SUN STORAGE

A STUDY ON PROPERTIES OF HYDROGEN ADMIXTURE IN POROUS UNDERGROUND-GAS-STORAGE FACILTIES BY MEANS OF AN IN-SITU EXPERIMENT

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Table of Contents

Background

The increasing roll-out of energy generation by volatile renewable sources (wind, solar) calls for the development of forward-looking and seasonal storage solutions. Underground Gas Storage facilities are already a save and reliable possibility to store large amounts of energy. A broadly discussed way to solve the challenge of storing renewable energy is the „Power to Gas"-technology. Using this technology makes it possible to transfer surplus electricity production, which cannot be fed into the power grid due to capacity bottlenecks or due to low consumer loads, into hydrogen or synthetic methane.

The tolerance of hydrogen in the existing natural gas infrastructure is the topic of numerous international research projects. The results of this research show the possibility to transport a share of several percent of hydrogen in natural gas without causing any harm to the transportation grid and the distribution infrastructure [1,2]. However, for the underground gas storage infrastructure only literature studies exist. These studies make reference to experience during the "city gas" era, or are reasoned by analogy to similar problems when storing CO_2. Additionally, examples from pure hydrogen technologies are being referenced[3,4,5]. The need for research is clearly documented (Fig.1). Up to now no experimental set-up was chosen to simulate actual reservoir conditions nor was there any attempt to do an in-situ field experiment.

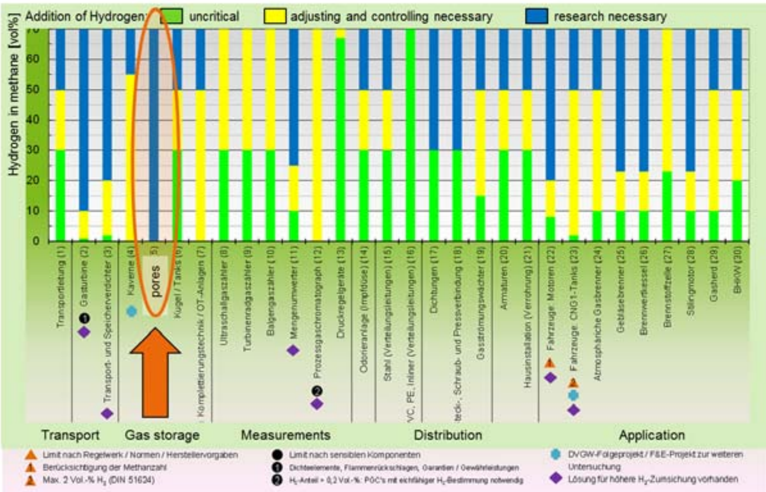


Figure 1: *H2-tolerance of selected items of the gas infrastructure [1] adapted by RAG.*

RAG is one of the major gas storage providers in Europe and has therefore a vital interest in positioning itself as a sustainable and economic energy service provider in a changing energy market. RAG operated storage infrastructure is located in Austria and consists of depleted porous gas reservoirs.

To achieve these goals and to use RAG's existing infrastructure in a future energy market, the research project "Underground Sun Storage" was initiated. A competent and experienced consortium was formed, consisting of several institutes of the "Montanuniversität Leoben" (MUL), the "University of Natural Resources and Life Sciences, Vienna, Department for Agrobiotechnology, IFA Tulln " (BOKU), the "Energieinstitut at the JKU Linz", Verbund AG and Axiom, a process engineering company. The research campaign is supported by the "Klima- und Energiefonds" of the Austrian government. Additionally international cooperation agreements with DVGW, NAFTA – a Slovakian Gas Storage operator and HYCHICO, an Argentinian Hydrogen storage project have been established.

Aim

The main objectives of this project are twofold. At first, the scientific focus of the project is to learn about the properties of hydrogen admixtures during operation of underground gas storage facilities. As a first experimental step, laboratory experiments and geochemical simulations have been carried out. In a second step, an in-situ field experiment will be conducted to show the possibility of storing renewable energies in porous subsurface storage formations and to verify the experimental results. The development of knowledge in this field is the basis to create new storage products, but there is also the necessity to be prepared in case the pressure to accept hydrogen at storage entry points will increase.

The other goal of this project is to show how the existing underground gas storage industry can contribute to a future energy system that relies on high shares of renewable energy production. It is already common knowledge that it is possible to store energy via the "power to gas" technology, using methanation to convert hydrogen into synthetic natural gas. However, the possibility to store and use hydrogen directly would be more efficient because one process step can be skipped and efficiency is better. So no matter whether the admixture of hydrogen is acceptable for storage operators or not, a technical solution for providing storage capacities can be offered.

Methods

Already during the development of the project, all involved partners agreed on a working plan. This project consists of two parts: laboratory experiments including mathematical simulations at various Universities and in-situ field experiments in a small depleted gas reservoir in Austria owned by RAG. The first milestone to achieve was to check the basic questions concerning outer integrity for RAGs storage facilities. Once this milestone was passed positively, the decision was taken to continue with design of the field experiment including all necessary technical equipment. The contact to all relevant public authorities was intensified. At the moment the approval process by public authorities is ongoing. Start of construction work is expected by end of April 2015.

The laboratory experiments conducted for this project cover the whole environment of sub-surface gas storage:

- Geochemistry, Geophysics
- Microbiological Processes in Subsurface Gas Storage Facilities
- Physical Behavior of Gasmixture under reservoir conditions (de-mixing and mobility effects)
- Material Science

For details about the laboratory experiments see the results section.

Since the outcome showed no indication that the integrity of the storage could be deteriorated, RAG started with detailed engineering of a field experiment at a preselected reservoir. The Underground Sun Storage project offers the unique opportunity to not only test the storage of hydrogen in a laboratory, but also at field level scale. The "real world" experiment will help to confirm the results of the lab tests and will give a further insight into the workings of the gas storage operation. RAG is able to conduct this in-situ test because in our portfolio a unique reservoir is present which is perfectly suited for such an experiment. What makes this depleted gas reservoir unique is on the one hand it's very small size (only ~5MMNm³ GIIP) and on the other hand that there is no known connection to any adjacent layer or aquifer. The reservoir is a litharenitic sandstone reservoir located in the Hall Formation in the upper Austrian molasse basin. The reservoir is at a depth of 1070m and a net pay zone of 1,5m which indicates the small size of the reservoir. The initial pressure was 107 bar(a). The seal is a shale layer of 50m thickness which prevents any communication with overlaying formations. This makes it an ideal "real world" laboratory for gas storage research at reasonable costs and time scales.

As a first step it was necessary to redefine the reservoir parameters as they might have changed during the production period. For this purpose pressure and temperature measurements have been conducted which proved the tightness of the reservoir (no pressure changes over the shut in period). Additionally it gave an indication that the reservoir is not influenced by any kind of aquifer. The next step was to conduct an injection and a production test to get a permeability measurement as well as an idea whether the well is suitable for gas injection, which was confirmed.

Furthermore the subsurface facilities have been tested on integrity (USIT-Cement Bond Log) and the completion of the well was changed following the regulatory guidelines for storage operations. To get a geochemical base line another water sample was taken previously to the start of injection so that any possible change in water composition could be monitored.

At the surface a small size storage plant has to be constructed. The main components are a 600kW electrolyzer unit (hydrogen production), a compressor unit with electrical drive, a gas mixing device and several control and measurement instruments for setting a certain hydrogen content and for balancing gas flows. Several auxiliary equipment units complete the setup of the plant. The nominal gas flow was set at 1.000 Nm³/h containing 90% of natural gas and 10% hydrogen. A share of 10% hydrogen is a generally discussed level throughout Europe. A higher share of renewable energy in the gas infrastructure could be realized by replacing natural gas with synthetic natural gas.

For the subsurface operation an injection and withdrawal profile was generated based on the data received from production and injection tests and limitations from the technical equipment. It was agreed to inject the gas mixture up to a surface pressure of 70 bar(g) (~75 bara reservoir pressure). The whole injection operation will be monitored via gas chromatograph in order to be sure about the volumes. Pressure and temperature will constantly be measured and monitored at the surface and subsurface. The injection phase will last about 3 to 4 months. After a shut in period of about 4 to 5 months the gas will be withdrawn again. The hydrogen content can be reduced to a level according to Austrian regulatory framework by blending with natural gas from nearby gas production before delivering it to the public distribution grid.

During production the gas chromatograph will be used to determine the amount of hydrogen produced in order to quantify any losses. Additionally, it is a test of mobility issue between different gases. If the gas produced at the beginning has a lower share of hydrogen than the gas at the end, it can be assumed that the hydrogen travels faster trough the formation than the natural gas.

During the shut in and production phase, water samples will be taken on a regular basis to monitor any changes of the chemistry in the reservoir. The monitoring of microbiological activity will also be a part of this investigation as the water samples are also monitored for microbiological growth.

Additionally a membrane separation for hydrogen of the company Axiom will be tested during production phase where its durability against high volumes and higher hydrocarbons can be verified.

Finally as an extension to the material experiments conducted in laboratories a test pipe will be installed at the well-site which will have slots to put material samples directly into the "wet" gas stream. This will allow us to test different materials under operating conditions.

Not only the technical, but also the economical, legal and environmental aspects of such a project are part of the research. A risk assessment is conducted parallel to this project including interviews with experts and literature reviews to define risks and opportunities of this technique. A "Life Cycle Assessment" and an analysis of the legal framework will complete the analysis within the research project.

Results

The Underground Sun Storage project is still in progress. Some experiments are finished already but interpretation is still going on. So the presented results below show tendencies to be confirmed with final reports.

Geochemistry, Petrophysics

Previously to the Underground Sun Storage project a research paper concerning the geochemical influence of hydrogen was conducted. It included a literature review and a simple geochemical simulation, which gave a first idea of hydrogen/methane storage and yielded promising results, which were part of the decision to conduct this project. The geochemical simulation showed, that over geological times, all hydrogen might eventually react with the subsurface environment (**Fig**. 2), but without generating any harmful gases (H_2S) or severe changes of the environment. The conclusion is that hydrogen reactions will be difficult to monitor, because the speed of the chemical reactions is very slow.

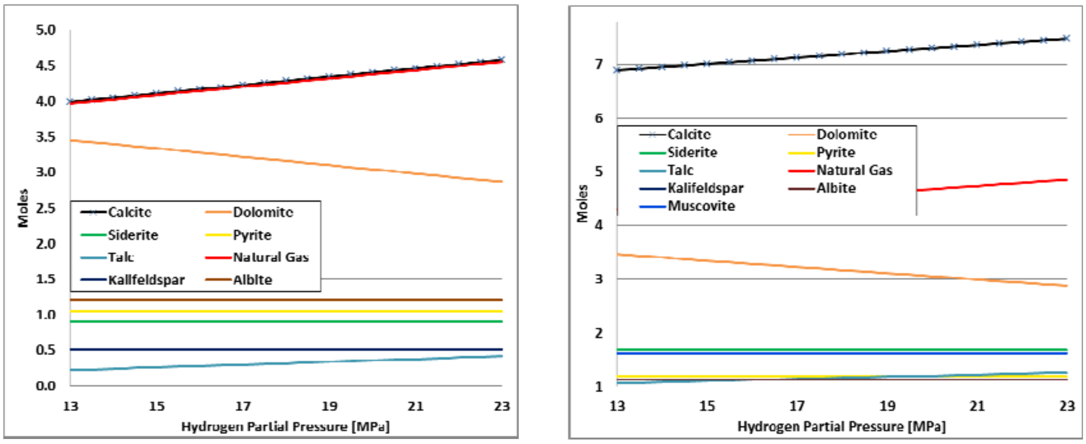


Figure 2: *On a long run, the injection of hydrogen influences the stability of minerals in the sub-surface formations. Here a geochemical simulation was conducted for two different mineralogical compositions, which both show the same trends. The results have been obtained via Gibbs Free Energy Minimization and display the equilibrium of the subsurface phases starting with a hydrogen share of 10% on the left hand side*[6]*.*

The research started in this paper is continued by Montanuniversität Leoben (MUL) and the DBI Leipzig on behalf of RAG to cover the preoperational part of dealing with geochemical issues. As an input for geochemical simulations done in Leoben the DBI in Leipzig conducted different flow experiments on cores from the reservoir and the overlying caprock as well as cement samples from RAG's facilities. The petrophysical parameters like permeability and porosity changes as well as the chemical parameters like rates of dissolution were provided to the reservoir engineering department of MUL. They will use these parameters to calibrate a reactive transport modeling program which will allow us to make predictions of the influence of hydrogen on our storage formations and ideally will also give a baseline for research on other reservoirs.

In a further step the tightness and resistivity of the cap rock against hydrogen intrusion and conversion was investigated. The cap rock is the overburden formation above a subsurface gas storage formation which prevents the gas from migrating out of the reservoir. It was found that the migration speed of hydrogen in the cap rock is in the same order of magnitude as monitored for methane which is very low and can therefore be technically neglected. Additionally no changes in the composition of the cap rock due to hydrogen could be monitored.

Finally flow experiments in cores from representative formations have been conducted to investigate whether the rock in the reservoir would be altered by hydrogen. To this point no changes either in permeability or in the chemical composition of the rocks could be observed. Therefore it can be assumed that in the short time of storage operations no significant changes will happen in the reservoir.

The experiments are accompanied by mathematical simulations conducted by MUL. The aim is to generate a geochemical simulation, which can model the changes in the water, gas and solid phase and predict the speed and severity of these reactions. For this purpose a geological model of the formation of interest (Haller Series) has been built via the software SKUA (Paradigm) to model the physical behavior (flow) of the hydrogen methane blend in the reservoir. Additionally a static geochemical model was generated via the Gibbs Free Energy Minimization software GEMS to model the long term changes in a hydrogen influenced reservoir. The static model showed the same results as were already gained in the research paper, namely that the hydrogen is reacting with the minerals from the reservoir.

The flow model and the geochemical simulation will, in a further step, be merged in order to create a reactive flow model which will then be used to verify the results from the lab and to make predictions what would happen to RAG's storage reservoirs if hydrogen is to be introduced. After the field test the results gained there will be implemented into the geochemical model as a calibration parameter.

Microbiological Processes in Subsurface Gas Storage Facilities

BOKU investigates the presence and activity of hydrogen consuming microorganisms in reservoirs. It is known from literature that several families of hydrogen metabolizing microbes may exist in subsurface formations [7,8,9]. In a first step, reservoir fluid has been taken from the formation of interest to investigate whether this environment was inhabited by microorganisms. Several families of microorganisms were found to be present in the reservoir with some of them being able to use hydrogen as a substrate.

In addition, the chemical composition of the formation fluid was analyzed by two different laboratories as a starting point for gas storage experiments. To establish experimental conditions as close as possible to the reservoir state, cores from offset wells in the Haller Series were inserted into bioreactors operated at reservoir temperature and pressure. After establishing a microbial consortium, a blend of methane, hydrogen and carbon dioxide has been introduced into the bioreactors and changes in composition have been monitored for several weeks. A change in the relative amount of gas components due to microbiological activity was observed accompanied by an increase of pH. To investigate whether these changes have an influence on the rock matrix, thin section and Xrf analysis have been conducted (Fig.3).

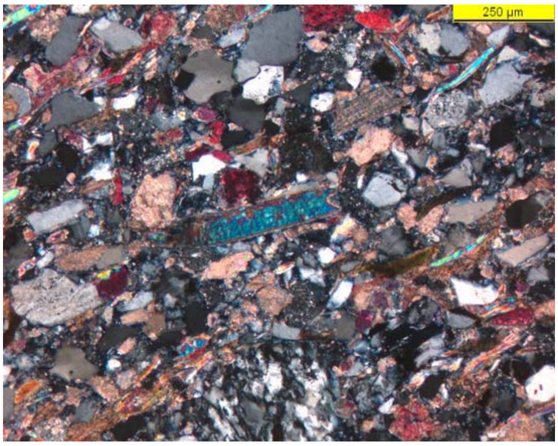


Figure 3: *Thin section of a litharenitic sandstone from an offset well with similar properties as the rocks forming the field test reservoir.*

At the grains and in the mineral matrix no changes could be observed which supports the assumption, that microbiologically induced alterations mainly influence the gaseous and aqueous phase. Some of the cores used in the reactor experiment showed embrittlement on the outside, but this effect could be explained by clay swelling.

Figure 4: *Bioreactors for testing microbiological activity under reservoir conditions at BOKU.*

Therefore, microbial activity could be confirmed for the experiments due to monitoring of pressure changes and gas composition (Tab. 1). Fortunately, no significant H_2S generation was detected in the gaseous phase.

Methanogenesis
$4H_2+CO_2 => CH_4 +2H_2O$
Homoacetogenesis
$2CO_2+4H_2 => CH_3COOH +2H_2O$
Sulphate reduction
$4H_2+SO_4^{2-}+2H^+ => H_2S +H_2O$

Tab.1*: Possible biochemical reactions which consume hydrogen.*

As mentioned before, results provided by the experiments of DBI showed a different picture. Here no changes in the phases could be detected. There was a slight increase of pH in the liquid phase which can be easily explained by the dissolution of hydrogen into the reservoir brine. Therefore it can be assumed that the geochemistry has only an insignificant influence on the storage operations within such a comparably short timeframe.

These claims are also supported by the abiotic experiments conducted by IFA. These experiments also showed only insignificant changes in the phase composition.

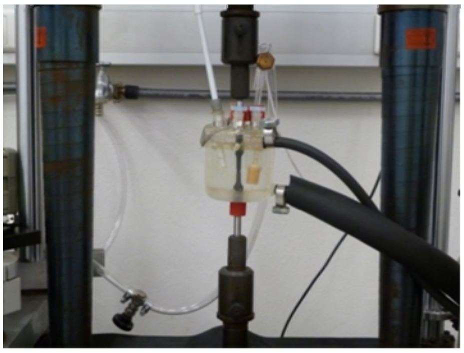
Physical Behavior of Gasmixture under reservoir conditions (de-mixing effects)

To get a more detailed approach towards de-mixing issues the MUL conducted further tests, which just dealt with the physical behavior of the gas mixture in a dry porous media. Here a blend of methane and hydrogen was investigated in a seven meter column filled with sand. The first run of experiments was static in order to determine whether de-mixing in the blend could happen during shut in of the storage because of gravitational effects. In this case, no de-mixing could be monitored. A second run of experiments was conducted dynamically. It is assumed that difference in molecule size of hydrogen and methane has an influence on the mobility of these two gases which would lead to de-mixing as the hydrogen travels faster through the porous media than the methane. The blend flowed through the columns and the composition was measured at the in- and outlet. Still no difference could be found which means that the mobility in this case seems to have an insignificant influence.

Material Science

First the stability of cement against hydrogen intrusion as well as change in composition has been investigated. The experiments showed that the cement is tight against hydrogen migration as it is tight against methane migration. However it was observed that the "Portlandite" which makes up the bulk of the cement was converted to "Vaterite". This mineral is slightly denser then the "Portlandite" and is generated by enclosure of CO_2 into the matrix of the "Portlandite". This effect is known as carbonatisation and happens due to pressure and temperature changes when cement is exposed to CO_2. Therefore an influence of hydrogen in this process can be expulsed. Still some shrinkage in volume occurred. However the majority of the volume shrinkage could be led back to compression issues. So there seems to be no problem with using the same cement as in other operations.

To round up the scientific laboratory work the resistivity of different steel qualities used in storage operations against corrosion or hydrogen induced fracking has been investigated. These experiments have been conducted by MUL. Steel grades tested had a tensile strength of up to 1100 N/mm². Molecular hydrogen causes no significant reduction of ductility at 10 bar partial pressure. Immersion tests showed that there was no hydrogen absorption. The results showed that the existing infrastructure and the materials used are compatible with a hydrogen gas environment[10].



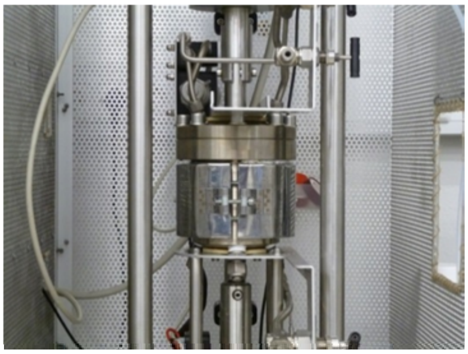


Figure 5: *Testing tensile strength under hydrogen influence at Montanuniversität Leoben.*

<u>In-situ field experiment</u>

All experiments conducted until now show that the chosen reservoir is suitable for operating a field test. The start of the test facility is scheduled in fall 2015.

Conclusion

With the Underground Sun Storage project RAG ensures the compatibility of its infrastructure for futures energy challenges. The results gained in the project will be essential for the further development in our gas storages and will determine the storage strategy in the following years. We are aware of the fact that all existing subsurface storage facilities have their own geological, geochemical and microbiological characteristics. Therefore we would like to encourage other storage providers to do similar experiments and research as we do in the Sunstorage project to get comparable results from other facilities. Our activities are only focusing on RAG's facilities, and with that only on the setting of our storage formations and materials.

The ongoing project already yielded promising results, which led to the decision of conducting the field test. Up to the present we do not expect any problems with storage integrity. Commercial and operational benefits and handicaps need to be evaluated after having finished the in-situ experiments. We do expect, however, that there will be the need for long term operational observation and experience.

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